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SYNTHESIS OF CATIONIC IRON COMPLEXES WITH THE CYCLOBUTENYLIDENE LIGAND. THE CRYSTALLINE STRUCTURE OF 1-TRIPHENYLPHOSPHONIUM-2-PHENYLVINYL-η^5-CYCLOPENTADIENYLDICARBONYLIRON TETRAFLUOROBORATE

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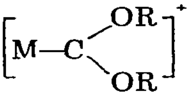
Summary

Stable, cationic, binuclear iron complexes with a new cyclobutenylidene bridge ligand $\{[Cp(CO)_2Fe]_2(Ph_2C_4H)\}^+ X^-$ ($X = ClO_4$, BF_4) have been obtained by protonating the σ-phenylacetylide iron complex $Cp(CO)_2FeC{\equiv}CPh$ with the strong protonic acids $HClO_4$ or HBF_4 in acetic anhydride. In the presence of PPh_3 this reaction results in the formation of metal—vinyl complexes containing the phosphonium cation $\{Cp(CO)_2Fe[C(PPh_3){=}CHPh]\}^+ X^-$ ($X = ClO_4$, BF_4). When $Cp(CO)_2FeC{\equiv}CPh$ reacts with $HClO_4$ or HBF_4 in benzene, acetone or alcohol, $[CpFe(CO)_3]^+ X^-$ ionic complexes ($X = ClO_4$, BF_4) are formed. The structure of the above compounds has been confirmed by IR, ^{1}H and ^{13}C NMR spectra and X-ray analysis.

Introduction

From the reactions of Pt [1] and Ni [2] acetylide complexes with alcohols in the presence of strong protonic acids (HPF_6 or HBF_4), cationic organoelemental compounds with the alkoxycarbene ligand,  $\left[M{-}C\begin{smallmatrix}OR\\OR\end{smallmatrix}\right]^+$ X^-, have been obtained. It was shown [3] that the alkoxycarbene ligand is formed via the intermediate vinylidene carbenium ion $Pt{-}C^+{=}CHR$, which is stabilized by the transition metal ion. Reactions of $Cp(CO)_2FeC{\equiv}CMe$ with $HClO_4$ or HBF_4 in benzene or ether result in the formation of ionic complexes $[CpFe(CO)_3]^+ X^-$ [4]. We have previously reported [5] * on the synthesis and structure of a stable, cationic,

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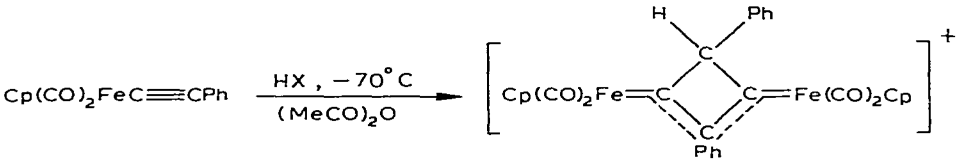
[*] After a preliminary report of our results was submitted for publication in Russian [5], and the present communication was prepared for this journal, Davidson and Solar published [12] their synthesis of the similar dimetallo-stabilized cyclobutenium ion but without the X-ray structural study.

binuclear iron complex with a new cyclobutenylidene bridge ligand, $\{[Cp(CO)_2Fe]_2(Ph_2C_4H)\}^+ ClO_4^-$, obtained from the reaction of $Cp(CO)_2FeC{\equiv}CPh$ (I) with $HClO_4$ in acetic anhydride. In the present work we discuss in greater detail the reactions of complex I with the strong protonic acids $HClO_4$ and HBF_4, and give the results of the X-ray analysis of the $\{Cp(CO)_2Fe[C(PPh_3){=}CHPh]\}BF_4$.

Results and discussion

The reaction of I with equimolal amounts of $HClO_4$ or HBF_4 in benzene, acetone or methanol at room temperature, results in the formation of $[CpFe(CO)_3]^+X^-$ iron complexes (where X = ClO_4 (II), BF_4 (III)), previously obtained by other methods [6,7]. The yields of II and III depend on the native of the solvent and increase as one passes from benzene to methanol, from 9 to 79%.

From the reaction of complex I with $HClO_4$ or HBF_4 in acetic anhydride (ratio of reagents 1/1), we obtained binuclear iron complexes with an unusual cyclobutenylidene bridge ligand (eq. 7.). Compounds IV and V are orange crystalline

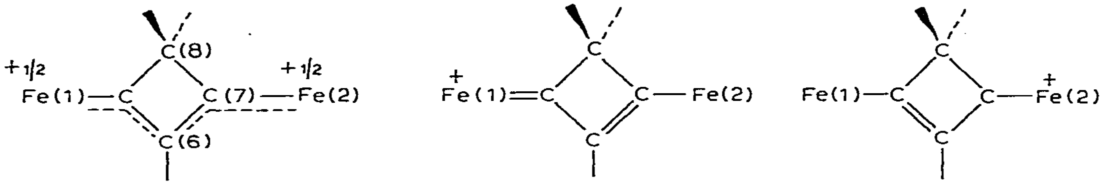


(1)

(X = ClO_4 (IV), 54%; BF_4 (V), 61%)

substances stable in air. They decompose at 120 and 160°C, respectively. Both compounds are moderately soluble in conventional organic solvents and insoluble in water. IR spectra of complexes IV and V (in CH_2Cl_2 solution) have $\nu(C{\equiv}O)$ absorption bands at 2010, 2045 and 2057 cm^{-1}. The ^1H NMR spectra of IV and V (in acetonitrile) have the following singlets: $\delta(C_5H_5)$ 5.20 and a multiplet with a centre $\delta(C_6H_5)$ 7.65 ppm (ratio of intensities 1/1). The ^{13}C NMR spectrum of complex V (Table 1) is consistent with the structure of this compound.

Based on the data of X-ray analysis [5], the central part of the cation is described well by combination A of canonical forms B and C.



(A) (B) (C)

The presence of the Fe(1)C(5)C(6)C(7)Fe(2) conjugation chain in the central part of the cation makes it possible to assume that the positive charge is delocalized between the two iron atoms.

The cyclobutenylidene ligand in complexes IV and V seems to originate via the mononuclear cation (D) stage. The formation of such a cation was previously

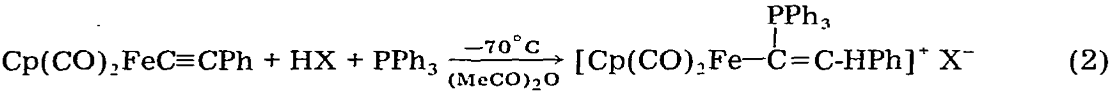
TABLE 1

^{13}C NMR SPECTRAL DATA OF COMPOUNDS V AND VII.

Complex	C_5H_5	CO	C(1)	C(3)	C(2)	C(4)	Ph
$\{[Cp(CO)_2Fe]_2(Ph_2C_4H)\}BF_4$	88.27	209.74	261.03				Multiplet in the region of 139.77—128.71
$[Cp(CO)_2Fe\overset{PPh_3}{C}(1)\text{—}C(2)PhH]BF_4$	86.54	168.64 168.24	213.41	—	119.30	—	Multiplet in the region of 134.13—122.94

assumed when studying the reaction of $Cp(CO)_2FeC{\equiv}CMe$ in an ethanol solution of hydrochloric acid [4].

Scheme 1 has been confirmed by the formation of phosphonium complexes VI and VII, resulting from the interaction of the σ-phenylacetylide complex of iron with the studied acids in acetic anhydride in the presence of PPh_3 (eq. 2).



$$Cp(CO)_2FeC{\equiv}CPh + HX + PPh_3 \xrightarrow[(MeCO)_2O]{-70^\circ C} [Cp(CO)_2Fe\text{—}\overset{PPh_3}{\overset{|}{C}}{=}C\text{-}HPh]^+ X^- \qquad (2)$$

($X = ClO_4$ (VI), BF_4 (VII))

Complexes VI and VII are yellow crystalline substances with melting points at 183—187°C (dec.) and 199—200°C (dec.), respectively. They are practically insoluble in water, aliphatic hydrocarbons, benzene and chloroform and moderately soluble in alcohols. The IR spectra of complexes VI and VII (in CH_2Cl_2) exhibits $\nu(C{\equiv}O)$ bands at 1980 and 2028 cm^{-1}. The Raman spectrum of VI has an intensive band at 1538 cm^{-1} that can be assigned to the valence vibrations of the C=C bond. ^{1}H NMR spectra of the complexes (in acetonitrile) contain a sharp singlet, $\delta(C_5H_5)$ 4.31 and a multiplet with a centre, $\delta(C_6H_5)$ 7.70 ppm. The chemical shifts of the ^{13}C NMR spectrum of complex VII are given in Table 1. The structure of VII has been determined by a comprehensive X-ray study. The crystals of VII are monoclinic, a = 12.050(3), b = 15.379(4), c =

(continued on p. 298)

SCHEME 1

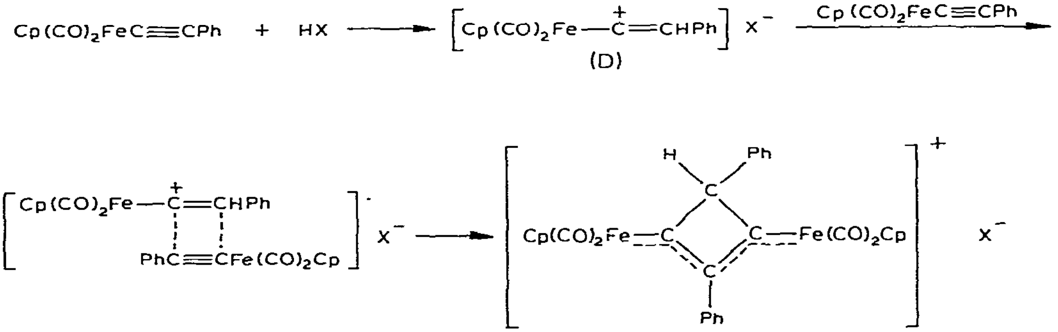


TABLE 2

COORDINATES OF ATOMS (Fe × 10^5, the others × 10^4) AND TEMPERATURE FACTORS (XIII) IN $T = exp[(-1/4)(B_{11}a^{*2}h^2 + ... + 2B_{12}a^*b^*hk + ...)]$ [a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	28377(8)	19411(7)	1972(5)	41(1)	47(1)	25(0)	10(1)	−4(0)	−6(1)
F	2685(1)	1902(1)	2225(1)	30(1)	31(1)	27(1)	0(1)	−1(1)	0(1)
C(1)	1150(5)	627(4)	359(4)	78(4)	53(4)	66(3)	−5(3)	−25(3)	0(3)
C(2)	1107(5)	3066(4)	−580(3)	74(4)	58(3)	57(3)	19(3)	−31(3)	−10(3)
C(1)	1831(7)	1156(5)	340(5)	56(5)	40(4)	39(4)	17(4)	−17(4)	−11(4)
C(2)	1805(7)	2655(5)	−289(4)	50(4)	49(4)	28(3)	4(4)	−10(3)	−10(3)
C(3)	2745(5)	2547(4)	1301(4)	27(3)	35(4)	22(3)	6(3)	−5(2)	0(3)
C(4)	2580(6)	3400(5)	1446(4)	39(4)	39(4)	25(3)	0(3)	−2(3)	4(3)
C(5)	2505(6)	4132(5)	853(4)	45(4)	34(4)	24(3)	−1(3)	−1(3)	−3(3)
C(6)	1571(6)	4651(5)	810(4)	57(5)	39(4)	32(4)	2(4)	−4(3)	1(3)
C(7)	1449(8)	5356(5)	270(5)	72(6)	47(5)	45(5)	5(4)	−3(4)	10(4)
C(8)	2282(10)	5552(6)	−220(5)	107(7)	48(5)	43(4)	3(5)	6(5)	16(4)
C(9)	3228(9)	5059(6)	−168(6)	87(7)	60(6)	64(5)	−10(5)	37(5)	18(5)
C(10)	3350(6)	4361(5)	373(5)	66(5)	49(5)	50(4)	0(4)	14(4)	5(4)
C(11)	2987(5)	2533(4)	3159(4)	36(3)	33(4)	23(5)	1(3)	2(3)	−5(3)
C(12)	2372(6)	2314(5)	3841(4)	51(4)	38(4)	34(3)	10(3)	5(3)	−2(3)
C(13)	2640(8)	2889(6)	4563(4)	84(6)	61(5)	27(4)	11(5)	13(4)	1(4)
C(14)	4488(8)	3484(5)	4604(5)	83(6)	43(4)	32(4)	1(4)	−11(4)	−5(3)
C(15)	4105(6)	3603(5)	3936(5)	54(4)	53(4)	36(4)	−4(4)	−6(3)	2(3)
C(16)	3858(6)	3115(9)	3219(4)	44(4)	45(4)	32(3)	7(4)	−2(3)	−2(3)
C(17)	1295(5)	1482(5)	2257(4)	28(3)	44(4)	29(3)	4(3)	1(3)	−2(3)
C(18)	403(6)	1969(5)	1894(4)	35(4)	55(4)	45(4)	5(4)	4(3)	2(4)

C(19)	−671(7)	1684(7)	1954(6)	31(4)	94(7)	62(5)	14(4)	3(3)	−1(5)
C(20)	−871(7)	944(8)	2380(6)	36(5)	112(8)	68(6)	−16(5)	11(4)	−9(6)
C(21)	7(8)	459(6)	2751(5)	55(5)	71(6)	63(5)	−19(5)	15(4)	1(4)
C(22)	1093(6)	733(5)	2697(4)	37(4)	47(4)	47(4)	−4(3)	10(3)	4(3)
C(23)	3243(5)	1002(4)	2280(4)	29(3)	38(4)	25(3)	7(5)	−2(2)	2(3)
C(24)	4712(6)	1114(5)	2668(4)	31(4)	44(4)	42(4)	1(3)	0(3)	2(3)
C(25)	5463(6)	429(6)	2700(5)	28(4)	68(5)	46(4)	14(4)	−1(3)	0(4)
C(26)	5195(7)	−356(5)	2345(5)	45(4)	56(5)	39(4)	24(4)	9(3)	−2(4)
C(27)	4144(7)	−478(5)	1950(4)	50(4)	40(4)	39(4)	11(4)	9(3)	−1(3)
C(28)	3366(6)	195(5)	1923(4)	39(4)	39(4)	32(3)	−1(3)	1(3)	−3(3)
C(29)	4416(8)	1361(10)	361(6)	54(5)	107(8)	44(5)	52(6)	11(4)	17(6)
C(30)	4544(8)	2208(10)	187(9)	45(5)	91(8)	84(8)	6(5)	18(5)	−32(6)
C(31)	4014(13)	2345(10)	−582(11)	109(11)	129(11)	94(10)	62(8)	72(9)	72(8)
C(32)	3555(12)	1603(17)	−378(7)	82(8)	273(22)	33(5)	78(12)	−1(5)	−54(9)
C(33)	3817(11)	970(7)	−292(12)	68(7)	75(7)	137(11)	8(6)	30(7)	−59(8)
B	1660(5)	1860(5)	7030(5)	72(3)					
P(1)	688(5)	1549(4)	6679(4)	97(2)					
P(2)	1602(6)	2398(6)	7704(5)	93(2)					
P(3)	2637(7)	1515(6)	7022(6)	71(2)					
P(4)	1766(9)	2636(7)	6542(6)	104(3)					
P(5)	2368(21)	2105(18)	6459(16)	89(6)					
P(6)	2195(12)	1047(9)	7275(9)	65(3)					
P(7)	1364(14)	1674(12)	7891(11)	108(5)					

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[a] For the atoms of BF_4 anion, B_{iso} ($Å^2$) are given.

16.165(5) Å, $\beta = 95.03(2)°$, D (det.) = 1.39, D(calc.) = 1.40 g cm^{-3}, $Z = 4$, space group $P2_1/n$. The structure has been deciphered with the help of the heavy atom method and refined by the least-squares method in anisotropic-isotropic (for BF_4^- atoms) full-matrix approximation to $R = 0.076$ for 2813 reflections with $|F| \geqslant 2\sigma$ (the experiment was performed on a "Syntex P2$_1$" diffractometer, λ(Mo-K$_\alpha$), graphite monochromator, $\nu/2\nu$ scanning, $2\nu \leqslant 50°$). The coordinates of atoms and the temperature factors are given in Table 2.

The structure of the $Cp(OC)_2Fe{-}C(P^+PPh_3){=}CHPh$ cation in VII is shown in Fig. 1, the bond lengths and valence angles are given in Table 3. The coordination of the iron atom is octahedral, i.e., the usual one for the monocyclopentadienyliron complexes of the $CpFe(CO)_2R$ type. The CFeC angles are in the range of 89.9(3)—96.3(3)°, mean distances for Fe—CO 1.76(1) and C—O 1.15(1) Å, are usual, average FeCO angle is 175(1)°. The average distances Fe—C(Cp) 2.09(1), and C—C(Cp) 1.36(2) Å (the latter are somewhat underestimated due to the considerable librational oscillations of the Cp ligand) are comparable to those found in other monocyclopentadienyl iron complexes (e.g., in I Fe—C(Cp) and C—C(Cp) are equal to 2.11(2) and 1.42(3) Å respectively, in *cis*-[(Cp)Fe-$(CO)_2]_2$ [8] to 2.11 and 1.41 Å, respectively).

The length of the σ-bond in Fe—C(3), 2.025(6) Å, is only slightly less than the normal length of the σ-bond in Fe—C(sp^2), 2.04 Å, in similar complexes [9]. The length of the uncoordinated double bond C(3)=C(4), 1.35(1) Å, is close to the standard value of 1.337 Å [10]. In accordance with the sp^2 hybridization of

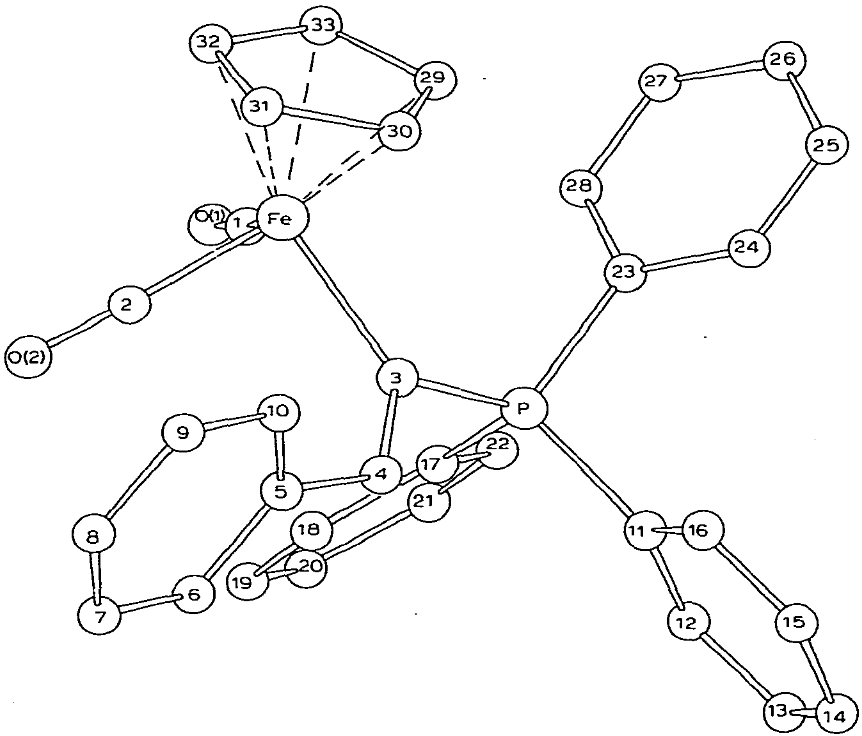

Fig. 1. The structure of $[Cp(CO)_2Fe{-}C(PPh_3){=}CHPh]^+$.

TABLE 3

BOND LENGTHS [a] AND VALENCE ANGLES OF $Cp(OC)_2Fe—C(PPh_3)=CHPh$

Bond	d(Å)	Bond	d(Å)	Angle	ω(°)
Fe—C(1)	1.741(9)	C(1)—O(1)	1.16(1)	C(1)FeC(2)	90.8(4)
Fe—C(2)	1.776(8)	C(2)—O(2)	1.14(1)	C(1)FeC(3)	96.3(3)
Fe—C(3)	2.025(6)	C(29)—C(30)	1.34(2)	C(2)FeC(3)	89.9(3)
Fe—C(29)	2.10(1)	C(29)—C(33)	1.37(2)	FeC(3)P	119.1(3)
Fe—C(3)	2.10(1)	C(30)—C(31)	1.36(2)	FeC(3)C(4)	128.4(5)
Fe—C(31)	2.07(2)	C(31)—C(32)	1.34(3)	PC(3)C(4)	112.0(5)
Fe—C(32)	2.08(1)	C(32)—C(33)	1.38(3)	C(3)C(4)C(5)	129.2(6)
Fe—C(33)	2.10(1)	C(3)—C(4)	1.35(1)	C(3)PC(11)	112.2(3)
P—C(3)	1.799(6)	C(4)—C(5)	1.48(1)	C(3)PC(17)	109.1(3)
P—C(11)	1.804(6)	C—C(Ph)	1.38(1)	C(3)PC(23)	113.1(3)
P—C(17)	1.800(7)			C(11)PC(17)	106.8(3)
P—C(23)	1.799(7)			C(11)PC(23)	106.9(3)
				C(17)PC(23)	108.5(3)

[a] The average length of the bond B—F in unordered BF_4^- is equal to 1.39(2) Å.

the C(3) atom, the sum of its valence angles is equal to 359.6°, and, due to the voluminosity of the $Cp(OC)_2Fe$ fragment, the FeC(3)C(4) and FeC(3)P angles are somewhat enlarged (128.4(5) and 119.1(3)°, respectively) when compared with the C(4)C(3)P angle of 112.0(5)°. The coordination of the P atom is distorted tetrahedral (CPC valence angles 106.8—113.1°) with the average length of the P—C bond equal to 1.801(6) Å, which is close to the normal P—C(sp^2) values in phosphonium salts (e.g., in $[Ph_3PCH_2Ph]^+Cl^-$ [11] the average length of the P—C(Ph) bond is equal to 1.790 Å).

Experimental

Perchloric and tetrafluoroboric acids of concentrations 57 and 40%, respectively, were used in the study. IR spectra were taken on a UR-20 "Zeiss" spectrophotometer, PMR spectra on a Hitachi-60 spectrometer with a solvent used as a reference standard. ^{13}C NMR spectra were obtained in CH_2Cl_2 on a "Bruker HX-90" spectrometer (22.635 Hz). The Raman spectrum was obtained on a PHO (Coderg) spectrometer with laser excitation. The melting points of compounds were obtained in sealed capillaries.

Synthesis of $\{[Cp(CO)_2Fe]_2(Ph_2C_4H)\}ClO_4$ *(IV)*

1.6 g (9 mmol) of $HClO_4$ in 1 ml of acetic anhydride was slowly added, with stirring, to a solution of 2.4 g (8.6 mmol) of $CpFe(CO)_2C{\equiv}CPh$ in 50 ml of acetic anhydride (—70°C). The solution was heated to room temperature and the solvent removed under vacuum. By recrystallizing the solid residue from ethanol, 1.53 g (54%) of orange crystals, decomposing without melting above 120°C, were isolated. (Found: C, 54.43; H, 3.62; Fe, 16.43; Cl, 5.38. $C_{30}H_{21}Fe_2O_8Cl$ (656.47) calcd.: C, 54.75; H, 3.35; Fe, 17.00; Cl, 5.40%.)

Synthesis of $\{[Cp(CO)_2Fe]_2(Ph_2C_4H)\}BF_4$ *(V)*

Obtained similarly to IV from 0.5 g (1.8 mmol) of I and 0.4 g (1.8 mmol) of HBF_4. 0.35 g (61%) of orange crystals, m.p. 160—161°C (dec.) were isolated.

Synthesis of $[Cp(CO)_2FeC(PPh_3)=CPhH]BF_4$ *(VII)*

1 g (3.6 mmol) of I dissolved in 25 ml of acetic anhydride was added with stirring, to a solution of 1.4 g (5.35 mmol) of PPh_3 and 0.9 g (4.1 mmol) of HBF_4 in 20 ml of acetic anhydride (—30°C). The solution was heated to room temperature and the solvent removed under vacuum. Excessive PPh_3 was washed away with hot hexane (2 × 20 ml) and the residue recrystallized from ethanol. 1.2 g (53%) of yellow crystals, m.p. 199—200°C (dec.) were isolated. (Found: C, 62.80; H, 4.12; Fe, 8.65; F, 12.14; P, 4.94. $C_{33}H_{26}FeO_2PBF_4$ (628) calcd.: C, 63.00; H, 4.13; Fe, 8.91; F, 12.10; P, 4.93%.)

Synthesis of $\{Cp(CO)_2Fe[C(PPh_3)=CHPh]\}ClO_4$ *(VI)*

Obtained in the same way as VII from 0.75 g (2.85 mmol) of PPh_3, 0.5 g (1.8 mmol) of I and 0.32 g (1.80 mmol) of $HClO_4$. 0.66 g (57%) of yellow crystals, dec. temp. 183—187°C, were isolated.

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